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Abstract

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ON THE NATURE OF THE ALKYLATION OF AROMATIC HYDROCARBONS BY OLEFINS IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

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In the opinion of most investigators, homologs of benzene react with olefins and other alkylating agents considerably faster than benzene itself ([1–3]). However, when the results of experiments are analyzed by means of equations describing consecutive processes ([4]), it is not difficult to see that this proposition is far from always justified. Very often, especially in the presence of acidic catalysts, benzene is alkylated more readily than monoalkylbenzenes, as a result of which the yield of the latter is higher than when $AlCl_3$ is used, although in the former case dealkylation of polyalkylbenzenes does not occur ([5,6]).

Proceeding from the most general ideas about the mechanism of the Friedel—Crafts reaction, one may suppose that the presence of alkyl groups in the benzene ring will strongly activate the substitution reaction only when the attacking agent possesses a substantial positive charge. Otherwise the activating effect of electropositive substituents will be manifested much more weakly; and since stereochemical and probability factors do not favor the alkylation of benzene homologs, benzene may then prove to be the more reactive compound.

To test this assumption and to establish a series of reactivities of alkylbenzenes, we studied the following reactions in the presence of $BF_3 \cdot H_3PO_4$: alkylation by propylene, cyclohexene, α-, β-, and isobutylenes of benzene and of binary mixtures of toluene with benzene, ethylbenzene, cumene, and o-, m-, and p-xylenes; alkylation by butylenes and cyclohexene of benzene with ethylbenzene, cumene, and xylenes; alkylation by propylene and β-butylene of m-xylene with sec- and tert-butylbenzenes; alkylation by cyclohexene of benzene with tert-butylbenzene; alkylation by propylene of cumene, diisopropylbenzene, and mixtures of the latter with benzene.

The starting aromatic hydrocarbons were chemically pure individual substances, whose physicochemical constants corresponded to the literature data. β-Butylene was isolated from the pseudobutylene-divinyl fraction; the remaining olefins were obtained by dehydration of the corresponding alcohols ([7]). The purity of the butylenes and propylene was 96-99% (analysis was carried out by the sulfuric-acid method ([7])); cyclohexene reacted quantitatively with a solution of bromine in chloroform. Before use, the n-butylenes were purified from possible isobutylene impurity by passing the gas through an air-lift and a bubbling column filled with 70-72% H_2SO_4. Alkylation was carried out by the previous method ([8]). For each experiment, 1 mole of aromatic hydrocarbons was taken. The reactivity of tert-butylbenzene toward n-olefins and cyclohexene was determined at 20°. The remaining experiments were carried out for 1-2 hr at 60° in the presence of 0.1 mole of $BF_3 \cdot H_3PO_4$ (unless the influence of various factors on the course of the process was being studied specially). Exceptions were the alkylation of benzene and of mixtures of aromatic hydrocarbons with isobutylene. In the first case the reaction conditions were as follows: temperature 35-40°, catalyst concentration 10 mol. %, time 1-1.5 hr; in the second, respectively: temperature 30°, 5 mol. % $BF_3 \cdot H_3PO_4$, and time 0.6-1 hr. All the results given in Tables 2 and 3 refer specifically to these standard conditions. The composition of the reaction products was established

by rectification on a 25-30 theoretical-plate column; the cyclohexene content in the benzene fraction was determined bromometrically or refractometrically. The total losses during treatment of the reaction mixture did not exceed 1-2% and did not alter the composition of the hydrocarbon layer at all, as was proved by control experiments. Therefore, in calculating the relative reactivities of aromatic hydrocarbons by the formula

$$r = \frac{K_A}{K_B} = \lg \frac{A}{A_0} \Big/ \lg \frac{B}{B_0},$$

where A_0 and A_B, B_0 and B are the initial and final amounts of the substances taken into the reaction, and K_A and K_B are the constants of the corresponding alkylation rates, we took the losses as proportional for all components of the hydrocarbon layer.

To determine the degree of influence of dealkylation on the composition of the alkylate, special experiments were carried out which showed that appreciable dealkylation is undergone only by hydrocarbons with tert-butyl groups. Moreover, the rate of this process depends only on the concentration of the substance being dealkylated and on the temperature. The dealkylation constant of di-tert-butylbenzene at 50° is 0.1 hr^{-1}, and at 30-35° it is 0.015-0.017 hr^{-1}. The other alkylbenzenes studied have constants of the order of 0.003-0.008 at 60-80° and, consequently, during the reaction time (1-2 hr) do not have time to undergo changes.

Identification of the alkylation products and determination of the orientation of substituents in polyalkylbenzenes were carried out both by the usual methods and with the aid of infrared absorption spectra.

Some experiments on the alkylation of a mixture of benzene and toluene with propylene are given in Table 1, which lists the values of the reactivity of toluene r, equal to the ratio of the rate constant for propylation of toluene to that of benzene.

Table 1

benzene	toluene	propylene	$BF_3 \cdot H_3PO_4$	Time, hr	benzene	toluene	cumene	cymene	polyalkylbenzenes	r
50	50	50	10	1.0	23.6	31.4	24.8	17.8	2.4	0.62
25	75	50	10	0.8	10.3	43.8	14.1	29.7	2.1	0.61
65	35	50	10	0.9	33.2	22.1	32.8	12.2	2.7	0.60
50*	50	55	10	2.0	21.3	29.3	25.6	18.8	5.0	0.63
50*	50	44	10	0.7	26.5	33.9	22.5	15.5	1.6	0.61
40	60	50	20	1.0	17.8	36.4	21.0	22.6	2.2	0.62
50	50	50	5	4.0	23.8	31.0	24.1	17.8	3.3	0.64
48	52	45	3	1.5	25.1	34.3	20.8	16.2	3.6	0.63
50	50	50	10	6.0	23.2	31.1	24.9	18.3	2.5	0.62
50	50	26	10	0.5	35.1	40.3	14.6	9.4	0.6	0.62
30**	30	30	10	1.2	14.5	19.0	–	–	–	0.63

* The reaction was carried out respectively at 30° and 80°; in the remaining cases, at 60°.

** Forty centimoles of cymene were added to the mixture being alkylated.

As is evident from these data, the reaction conditions and the ratios of the reagents do not exert a strong influence on the value of r. Similar results were also obtained in the alkylation of other hydrocarbons with propylene, *n*-butylenes, and cyclohexene. Only in the case of the reaction of benzene and its homologues with isobutylene was some influence of temperature and experiment duration on the ratios of the rate constants observed; this is associated with disproportionation of tertiary butyl groups and, possibly, with a greater difference in the activation energies of the competing reactions.

The values of the relative reactivities of benzene homologues with respect to various olefins are summarized in Table 2.

Table 2

Aromatic hydrocarbon	Propylene	β-Butylene	α-Butylene	Isobutylene	Cyclohexene
Toluene	0.62	0.56	0.72	3.78	0.94
Ethylbenzene	0.35	0.29	0.38	3.04	0.61
Isopropylbenzene	0.19	0.17	0.20	2.15	0.34
sec-Butylbenzene	0.17	0.16	0.17	–	–
tert-Butylbenzene	0.14	0.12	–	0.89	0.23

Aromatic hydrocarbon	Propylene	β-Butylene	α-Butylene	Isobutylene	Cyclohexene
o-Xylene	0.45	0.40	0.49	7.51	1.07
m-Xylene	0.38	0.31	0.39	0.68	0.58
p-Xylene	0.32	0.26	0.34	0.0	0.46

* Rate of alkylation of benzene = 1.

Table 3

Composition of the products of alkylation of aromatic hydrocarbons*

Alkylated compound	Olefin	Molar ratio of olefin to aromatic hydrocarbon	Benzene, exp.	Benzene, calc.	Monoalkylbenzenes, exp.	Monoalkylbenzenes, calc.	Dialkylbenzenes, exp.	Dialkylbenzenes, calc.	Trialkylbenzenes, exp.	Trialkylbenzenes, calc.	Tetraalkylbenzenes, exp.	Tetraalkylbenzenes, calc.
Benzene	Propylene	0.20	80.5	80.4	19.0	19.2	0.5	0.4	–	–	–	–
Benzene	Propylene	0.50	52.9	52.7	43.9	44.3	3.2	3.0	–	–	–	–
Benzene	Propylene	1.00	16.0	16.2	68.1**	67.7	15.9	15.6	–	0.5	–	–
Benzene	Propylene	1.55	0.9	1.0	51.4	51.1	40.2	41.0	6.8	6.5	0.7	0.6
Benzene	Propylene	2.21	–	–	16.3	14.6	51.3	52.5	27.5	28.2	4.9	4.7
Isopropylbenzene	Propylene	0.57	–	–	50.1	50.1	43.0	42.9	6.5	6.7	0.4	0.3
Isopropylbenzene	Propylene	1.20	–	–	12.8	12.6	51.2	51.8	30.4	30.1	5.6	5.5
Diisopropylbenzene	Propylene	0.32	–	–	–	–	70.5	70.6	27.0	26.8	2.5	2.6

Alkylated compound	Olefin	Molar ratio of olefin to aromatic hydrocarbon	Benzene, exp.	Benzene, calc.	Monoalkylbenzenes, exp.	Monoalkylbenzenes, calc.	Dialkylbenzenes, exp.	Dialkylbenzenes, calc.	Trialkylbenzenes, exp.	Trialkylbenzenes, calc.	Tetraalkylbenzenes, exp.	Tetraalkylbenzenes, calc.
Benzene and diisopropylbenzene (69.6 : 30.4)	Propylene	0.50	25.6	25.6	39.4	39.4	33.8	—	1.2	—	—	—
Benzene	β-Butylene	0.24	76.2	76.2	23.2	23.2	0.6	0.6	—	—	—	—
Benzene	α-Butylene	0.86	24.8	25.0	64.9	64.5	10.3	10.5	—	—	—	—
Benzene	β-Butylene	0.45	57.5	57.6	40.5	40.3	2.0	2.1	—	—	—	—
Benzene	α-Butylene	1.34	2.2	2.4	62.0	61.6	35.8	36.0	—	—	—	—
Benzene	Isobutylene	0.34	70.6	70.7	24.8	24.7	4.6	4.6	—	—	—	—
Benzene	Isobutylene	0.66	51.1	51.3	35.9	35.5	13.0	13.2	—	—	—	—
Benzene	Cyclohexene	0.35	67.2	67.3	30.9	30.7	1.9	2.0	—	—	—	—
Benzene	Isobutylene	0.97	22.6	22.4	58.3	58.7	19.1	18.9	—	—	—	—

* The relative reactivities of cyclohexylbenzene, tert-butylbenzene, sec-butylbenzene, and mono-, di-, and triisopropylbenzene in the corresponding reactions are respectively: 0.31; 0.89; 0.116; 0.185; 0.074; 0.037. The calculation was carried out by equations describing consecutive reactions (4).

** Experimental data borrowed from Topchiev and co-workers (9).

The catalyst $BF_3 \cdot H_3PO_4$ not only does not itself cause strong disproportionation of primary and secondary alkyl radicals, but also, in the course of the alkylation reaction, does not form "special complexes" that dealkylate polyalkylbenzenes.

Indeed, additions of the latter to the mixture being alkylated not only do not increase the yield of monoalkylbenzenes (5), which could also occur as a result of polymerization of the olefin or alkylation of part of the added substance, but also do not change the ratios of the rate constants calculated from the composition of the reaction mixture (see Tables 1–3). Moreover, the values of r were expressed by the same numbers (within the experimental error of $\pm 2\%$) regardless of the mixtures by whose alkylation they were determined, i.e., the so-called solvent effect in this case did not exert a substantial influence. This fact found confirma-

···also in the alkylation of individual hydrocarbons by olefins: the ratios of the rate constants of consecutive reactions do not depend on the depth of alkylation of the aromatic hydrocarbon (see Table 3), which makes it possible to predict the composition of the alkylate with sufficient accuracy.

If "external" factors have almost no effect on the relative rates of reactions of benzene homologs, then the nature of the alkylating agent determines these quantities no less than does the structure of the aromatic hydrocarbon itself. Most of the alkylbenzenes we have studied are alkylated by isobutylene much more readily than benzene, despite the practically complete absence of butylation in the *o*- and *m*-positions relative to the alkyl group. Propylene, *n*-butylenes, and cyclohexene, on the contrary, react faster with benzene than with its homologs. In all cases the Baker–Nathan series, determined to a considerable extent by hyperconjugation, is observed. We shall not undertake a detailed discussion of the hyperconjugation effect, since this question is not new. We shall point out only that the groundlessness of the views of those authors who explain differences in the alkylation rates of toluene, ethylbenzene, cumene, and *tert*-butylbenzene by difficulties arising during alkylation in the *o*-position[1] is very clearly emphasized by the results of alkylation of these hydrocarbons with isobutylene (see above). To interpret a number of regularities—above all the greatly reduced activity of the *m*-positions of alkylbenzenes (in comparison with any of the six positions of benzene), as well as the small values of the relative alkylation rates of cumene and butylbenzenes by *m*-olefins—it must be recognized that alkyl groups create hindrance not only in ortho but also in meta and para substitution (this is probably connected with impeded solvation of the transition complex). Naturally, owing to the increase in the electron-cloud density in the alkylbenzene molecule and the ready polarizability of the latter at the moment of reaction, the influence of unfavorable factors will be smoothed out and even overbalanced. On the whole, however, alkylbenzenes can react faster than benzene only with those olefins that are strongly polarized by the catalyst, forming ions with a large effective positive charge concentrated on the reacting carbon atom. Indeed, among the olefins we have studied, isobutylene alone, whose easy polarizability is well known, preferentially alkylates benzene homologs. On passing to cyclohexene and then to α-butylene, propylene, and β-butylene, the values of r decrease regularly, which is explained by a decrease in the activity of the attack-

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[1] G. E. Condon, *J. Am. Chem. Soc.*, **70**, 2265 (1948).

ing agents. The difference in the relative reactivities of alkylbenzenes toward α- and β-butylenes deserves special attention. This fact convincingly shows that cleavage of the π bond in the course of alkylation proceeds gradually, as the bond with the aromatic nucleus is formed. If the polarization of the olefins went as far as the formation of free carbonium ions, the indicated difference could not be observed, since both butylenes in the limiting case give identical ions. In our opinion, it is precisely in the hidden-ionic mechanism of the alkylation reaction that the specificity of the catalytic action of $BF_2 \cdot H_3PO_4$ and of certain other acid catalysts lies.

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REFERENCES

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